

(19) Japanese Patent Office (JP) (12) PATENT JOURNAL (A) (11) Kokai Patent Application  
No. HEI 9[1997]-24260

(43) Publication Date: January 28, 1997

Technical Disclosure

(51) Int. Cl. <sup>6</sup> :	Sequence Nos. for office use:	FI
B 01 D 71/64		B 01 D 71/64
		71/40
D 01 F 6/78		D 01 F 6/78

Examination Request: Not requested

No. of Claims: 10 OL (Total of 14 pages)

(21) Application No.: H7[1995]-175923

(22) Application Date: July 12, 1995

(72) Inventor: Masayoshi Takatake  
801 Grace Nishi Chiba,  
2-8-6 Matsunami, Chuo-ku  
Chiba-shi, Chiba-ken

(72) Inventor: Hirotomo Nagata  
Dainippon Ink  
2-303 Sakura company residence  
3-5-1 Osakidai, Sakura-shi  
Chiba-ken

(71) Applicant: 000002886  
Dainippon Ink & Chemical, Inc.  
3-35-58 Sakanoshita,  
Itabashi-ku, Tokyo

(74) Agent: Katsutoshi Takane, patent attorney

(54) POLY(IMIDAZOPYRROLONE-IMIDE) COPOLYMER SEPARATION MEMBRANE AND ITS  
PRODUCTION METHOD

(57) [Abstract]  
[Objective]

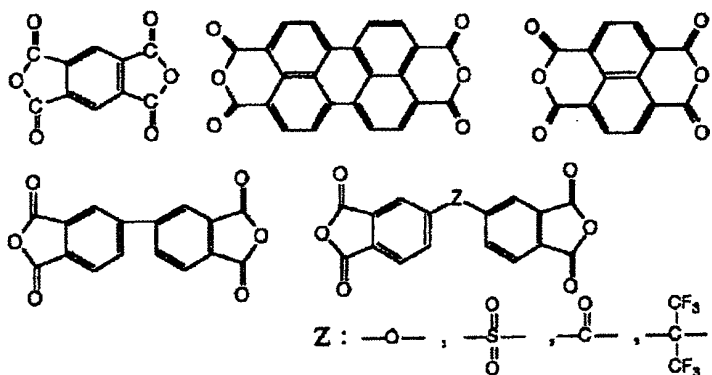
[Constitution] To provide a separation membrane having a close [= fine, dense] layer of a poly (imidazopyrrolone-imide) copolymer which is obtained by respectively using a specific tetracarboxylic acid dianhydride (A), a specific tetraamine (B) in equivalent molar quantity with (A), and a specific diamine (C) as an essential component, and applying these compounds to polycondensation of the amine component (D).

[Effectiveness] It exhibits excellent gas permeation and separability, and has excellent flexibility and is a usable film in practice.

[Claims]

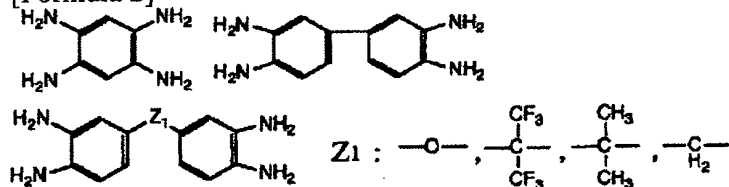
[Claim 1]

[Formula 1]

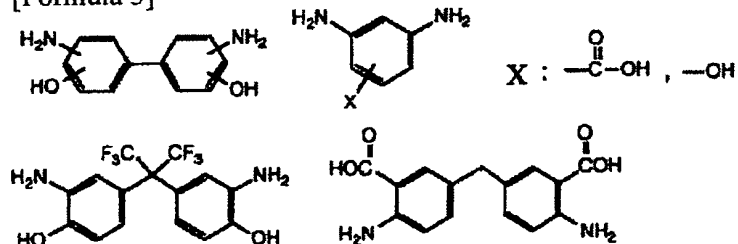


A poly (imidazopyrrolone-imide) copolymer separation membrane characterized by having a close layer containing a poly (imidazopyrrolone-imide) copolymer formed by allowing condensation polymerization of an equivalent molar quantity of amine component (D) with tetracarboxylic acid dianhydride (A), containing at least one kind of tetracarboxylic acid dianhydride (A) chosen from formula 1, at least one kind of tetraamine (B) chosen from formula 2, and at least one kind of diamine (C) chosen from formula 3 as the necessary components.

[Formula 2]



[Formula 3]



[Claim 2] A separation membrane as set forth in Claim 1, wherein the tetracarboxylic acid dianhydride (A) is 4,4'-(hexafluoroisopropylidene) diphthalic acid dianhydride, the tetraamine (B) is at least one kind of tetraamine chosen from 3,3', 4,4'-tetraaminobiphenyl, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminodiphenyl ether from formula 2, and the diamine (C) is at least one kind of diamine chosen from 4,4'-(hexafluoroisopropylidene) bis [2-amino-phenol], 3,3'-dihydroxy-4,4'-diaminobiphenyl, 3,3'-diamino-4,4'-dihydroxybiphenyl.

[Claim 3] A separation membrane as set forth in Claim 1 or 2, wherein the mole ratio of the tetraamine (B) and diamine (C) is 7/3~3/7, and the total molar quantity of the tetraamine (B) and diamine (C) is 30%~100% of the total molar quantity of the amine component (D).

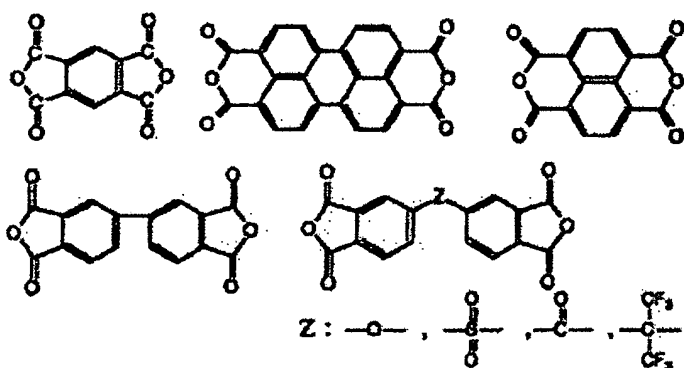
[Claim 4] A separation membrane as set forth in Claim 1~3, wherein the separation membrane

is a hollow fiber composite membrane.

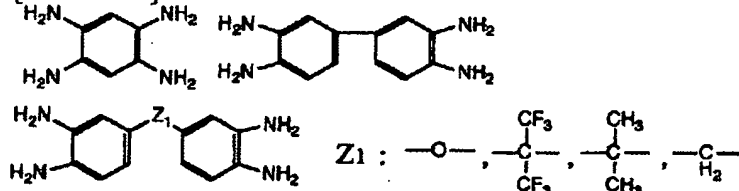
[Claim 5] A separation membrane as set forth in Claim 4 characterized in that the resin forming the porous supporting layer is a mixture containing at least one kind of resin chosen from a polyimide resin, a polysulfone resin, a polyether imide resin, a polybenzimidazole resin, and an aromatic polyamide resin.

[Claim 6]

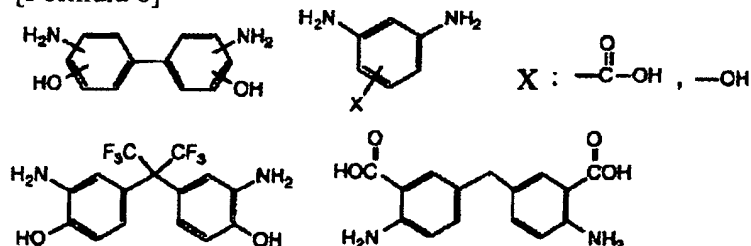
[Formula 4]



[Formula 5]



[Formula 6]



A production method of poly (imidazopyrrolone-imide) copolymer hollow fiber composite membrane having a close layer composed of a poly (imidazopyrrolone-imide) copolymer characterized by containing at least one kind of tetracarboxylic acid dianhydride (A) selected from formula 4, at least one kind of tetraamine (B) selected from formula 5, and at least one kind of diamine (C) selected from formula 6 as the required components, the tetracarboxylic acid dianhydride (A) is polymerized with the amine component (D) at the molar quantity equal thereto, the solvent soluble poly (imidazopyrrolone-imide) copolymer precursor dopant (a) and the dopant (b) of the polymer for the purpose of forming a porous supporting layer are

coextruded to a multilayer construction hollow yarn shape at the same time by using a multiple annular nozzle; then, after contact with a congealed liquid and coagulation, the poly (imidazopyrrolone-imide) copolymer precursor is subjected to poly (imidazopyrrolone-imide) copolymerization by heating.

[Claim 7] A production method as set forth in Claim 6, wherein the tetracarboxylic acid dianhydride (A) is 4,4'-(hexafluoroisopropylidene) diphthalic acid dianhydride, the tetraamine (B) is at least one kind of tetraamine chosen from 3,3', 4,4'-tetraaminobiphenyl, 1,2,4,5-tetraaminobenzene, 3,3',4,4'-tetraaminodiphenyl ether, and the diamine (C) is at least one kind of diamine chosen from 4,4'-(hexafluoroisopropylidene) bis [2-amino-phenol], 3,3'-dihydroxy-4,4'-diaminobiphenyl, 3,3'-diamino-4,4'-dihydroxybiphenyl.

[Claim 8] A production method membrane as set forth in Claim 6 or 7, wherein the mole ratio of the tetraamine (B) and diamine (C) is 7:3~3:7, and the total molar quantity of the tetraamine (B) and diamine (C) is 30%~100% of the total molar quantity of the amine component (D).

[Claim 9] A production method membrane as set forth in Claims 6~8, wherein the resin dopant (b) for forming the porous supporting layer is a mixture comprising at least one kind of resin chosen from the polyamide resin, polysulfone resin, polyether imide resin, polybenzimidazol resin, and aromatic polyamide resin.

[Claim 10] A production method membrane as set forth in Claims 6~9, wherein heating is conducted under reduced pressure or inert gas atmosphere at 250°C~400°C.

[Detail Description of the Invention]

[0001]

[Industrial Field of Application] The present invention relates to a separation membrane having a close layer composed of a poly (imidazopyrrolone-imide) copolymer with excellent gas permeation, separability, flexibility, solvent resistance, heat resistance, and durable properties when used as a gas separation membrane suitable for gas-gas and liquid-gas separation.

[0002]

[Prior Art]

[0002] Material separation through the intervention of a film is advantageous in [terms of] energy as compared with other separation approaches. It is actively applied to various industrial fields because of its characteristics, such as the equipment being small in size and light in weight, and the mechanism being simple and maintenance free. The separation membrane of the present invention has been utilized in the areas of, for example, oxygen/nitrogen separation of air, separation and recovery of hydrogen from drilling platform off-gas, separation and recovery of hydrogen in ammonia synthesis, recovery of carbon dioxide and removal of nitrogen oxides and sulfur oxide from the waste gas produced during thermal electric power generation and garbage incineration, recovery of carbon dioxide from oil field off-gas, removal of acids such as carbon

dioxide and hydrogen sulfide and of moisture (steam) from natural gas, recovery of methane and decarbonation of the landfill gas, dehumidification of air and organic vapor, anhydration of organic aqueous solution, separation of water from alcohol, pervaporation separation of volatile-matter liquor mixtures such as removal of water from esterification reaction systems, removal of gas dissolved in liquid, and dissolving of specific gas in a liquid etc. Of course, the present invention is not limited to these applications.

[0003]

[Prior Art] The basic requirements of a separation membrane are (1) the separability of the target separation object from the other component, (2) substance permeability, and (3) the membrane strength, heat resistance, durability, and solvent-resistance, etc. The membranous substance permeability is realized by means of the required membrane area, the membrane module, and the device size. Thus, the performance is realized by the features that primarily influence the initial cost, and the industrially practical usability is realized through development of the raw material with high permeability, and reduction of the thickness of the film of the active separation layer (close layer). On the other hand, the separability of the membrane is essentially the innate characteristics of the membrane in the case of the close layer membrane, and the characteristics influence the yield of the separation material. That is, it is the property determining the running cost.

[0004] Generally the material separation property and permeability of a polymer membrane have an inverse relation, and a polymer raw material with high permeability has low separability (it may also be referred to as selectivity). Therefore, the development of an excellent separation membrane requires the development of a membrane raw material with a good balance of the two conflicting properties. Moreover, development of the best film production method using this membrane raw material is essential.

[0005] In recent years, there have been a few reports about the probability of polyimidazopyrrolone having excellent gas permeability and selective balance when used as a gas separation membrane raw material.

[0006] For example, the draft collection on polymers (Polymer Preprints, Japan) Vol. 41, No. 3, page 644 (1992) reported several types of polyimidazopyrrolone with excellent gas selective permeability basic properties. Journal of Membrane science 55, pages 99-117 (1991) and Polymer Journal Vol.23, No.5, pages 481-490 (1991) also reported the specific polyimidazopyrrolone obtained by carrying out condensation polymerization of several types of polyamide with 4,4'-(hexafluoroisopropylidene) diphthalic acid dianhydride (hereinafter called as 6FDA) and tetraaminodiphenyl ether

[0007] Although the poly(imidazopyrrolone-imide) copolymer separation membrane [produced] by the condensation polymerization of 6FDA, 4,4' - oxydianiline, 3,3',4,4' - tetramino diphenyl

ether is stated to WO 94/12465, there is absolutely no mention of the diamine component indispensable in this invention.

[0008] Moreover, research is actively being pursued into a composite membrane composed of a close layer and a porous layer of essentially different raw materials which has a good balance of the various properties required for a separation membrane, and which can be mass produced satisfactorily.

[0009] For example, Kokai No. 49-62380 disclosed a method for producing a reverse osmosis membrane having a close layer and a porous layer composed of the same type or different types of polymer [formed] by coextrusion. In addition, the application of the gas separation membrane produced by this production method is described in The Gas Separation Development Technology, Toray Industries Research Center, page 39 (July 25, 1990 Issue).

[0010] Kokai No. 62-191019 disclosed a method of producing a hollow yarn separation membrane having multiple layers which are obtained using multiple resin solutions including the cellulose ester series resins such as cellulose acetate, cellulose triacetate, nitrocellulose; the polyamide series resins, and the polyester series resins with various concentrations between 30~60 wt%, and extrudes the resin solutions while successively increasing the concentration from the inside of the opening yarn spinning concentrically.

[0011] Kokai No. H1-99616 disclosed a method of producing a polyamide hollow yarn separation membrane with excellent reproducibility by extruding a low concentration polyamide solution, with a concentration of 0.1~20 wt.%, from the external toric opening of an internal toric type fiber spinning nozzle, which has a concentric opening, and a high concentration polyamide solution with a concentration of 10~50 wt.% and at least 1 wt.% higher than the low concentration polyamide solution, from the internal toric type opening part, at the same time.

[0012] Kokai No. H2-169019 disclosed a method of producing a hollow yarn membrane with a two-layer structure by extruding two different types of aromatic polyimide solutions from a wet yarn spinning nozzle having a concentric opening, such that the polyamide with a concentration of 7~25 wt.% is supplied from the external toric opening part, and the polyamide with a low concentration of 5~25 wt.% is supplied from the inner toric opening part, at the same time. To carry out wet yarn spinning, the asymmetric outer layer formed with the homogenous surface layer (close layer) and the integrated porous layer, and the porous only inner layer, are formed in an integrated body in a concentric shape.

[0013] Kokai 4-277019 disclosed a gas separation composite membrane using the specific polyamide resin and the specific polyimide resin produced according to the well known co-extruding method as the production method of the composite membrane.

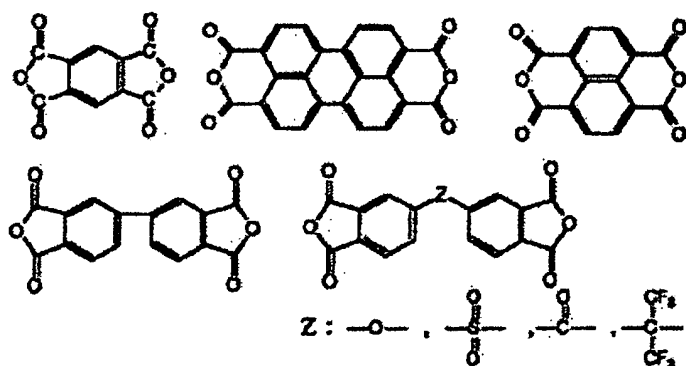
[0014] [Problems that the Invention is to Solve] Although the aforementioned polyamide or poly(imidazopyrrolone-imide) copolymer has comparatively satisfactory balance between gas

permeability and separability, the separability is insufficient when it is used as, for example, an air separation membrane, oxygen enrichment membrane, or nitrogen enrichment membrane. The aforementioned poly imidazopyrrolone resin generally lacks flexibility, turns into a gel easily, or has poor polymerization properties, and has inadequate mechanical properties required in the membrane raw material for production. Therefore, this raw material has not yet been utilized in practice for a gas separation membrane.

[0015] [Means for Solving the Problem] As a result of concerted research for the purpose of obtaining an excellent gas separation membrane, the inventors of the present invention found that by copolymerization of the specific tetracarboxylic acid dianhydride (A) with the amine component (D) containing the specific tetramine and the specific diamine as the required components, the poly (imidazopyrrolone-imide) copolymer exhibits excellent gas permeation and separability, and has excellent flexibility, heat resistance, and solvent resistance, which is suitable in a film for practical use, and thus completed the present invention. That is, the first invention of this application is the following.

[0016].

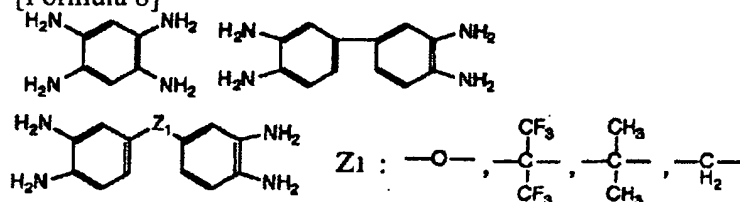
[Formula 7]



[0017] [text incorporated in paragraph 0021 due to Japanese text structure]

[0018]

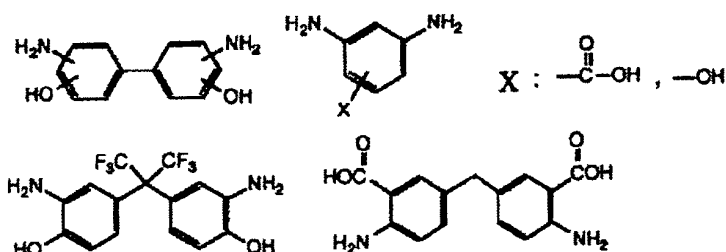
[Formula 8]



[0019] [text incorporated in paragraph 0021 due to Japanese text structure]

[0020]

[Formula 9]



[0021] The present invention relates to a poly (imidazopyrrolone-imide) copolymer characterized by having a close layer composed of a poly (imidazopyrrolone-imide) copolymer that has undergone condensation polymerization of the amine component (D) containing at least one kind of tetracarboxylic acid dianhydride (A) selected from formula 7, at least one kind of tetraamine (B) selected from formula 8 at a molar quantity equal to tetracarboxylic acid dianhydride (A), and at least one kind of diamine (C) selected from formula 9 as the required components.

[0022] This invention is explained in further detail below. The poly (imidazopyrrolone-imide) copolymer stated in the present invention is a polymer with the imidazopyrrolone structure, and a so called ladder-like combining area; the combining area has an imide structure mixed in the molecular chain, and has sufficient molecular weight for the formation of a delicate and thin film. This polymer is generally obtained by adding at least one kind of reaction auxiliary agent such as, for example, an acetic anhydride, a thionyl chloride, a trifluoroacetic acid anhydride, a cyclocarbodiimide, a pyridine, a triethylamine, and a benzoic acid in an adequate solvent such as N,N-dimethylacetamide, N-methyl pyrrolidone if necessary, and allowing polymerization of the tetracarboxylic acid dianhydride (A) with the amine component (D) (with mixture of tetraamine (B) and diamine (C) as the required components) at the molar quantity equal thereto. The precursor of the soluble copolymer which is essentially capable of being formed into a membrane and is substantially soluble in a solvent is heat-treated at a suitable temperature; furthermore, the precursor is cyclized and formed into a close layer. As the precursor of the soluble copolymer, any structure is acceptable if it meets the requirement which is essentially the capability to be formed into a membrane, and is substantially soluble in a solvent, and generates the poly (imidazopyrrolone-imide) copolymer by heating at an adequate temperature; for example, there are the polymers having at least one kind of structure such as polyamide, polyimide, polyisoimide, and polymidazol. The present invention includes, but is not limited to, these examples.

[0023] The tetracarboxylic acid dianhydride (A) used in polymerization of the poly (imidazopyrrolone-imide) copolymer which forms the close layer of the separation membrane of the present invention is at least one kind of tetracarboxylic acid dianhydride chosen from 6FDA, pyromellitic dianhydride, 3,3',4,4'-biphenyl tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3',4,4'-biphenyl sulfone tetracarboxylic

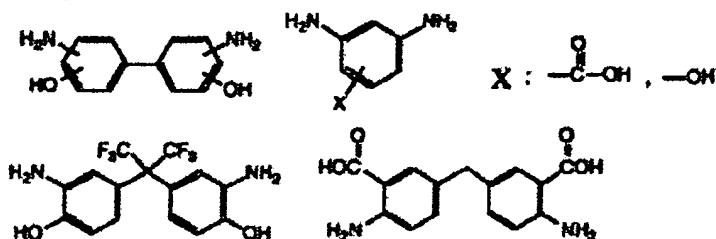


dianhydride, 3, 3', 4, 4'-diphenyl ether tetracarboxylic dianhydride, naphthalene- 1, 2, 4, 5-tetracarboxylic dianhydride, 3,4,9,10- perylene tetracarboxylic dianhydride, preferably 6FDA.

[0024] The tetraamine (B) is at least one kind of tetraamine chosen from 3,3', 4,4'-tetraaminodiphenylether, 3,3', 4,4'-tetraaminodiphenylmethane, 3,3', 4,4'-tetraaminobiphenyl (hereinafter abbreviated as diaminobenzidine), 1,2,4,5-tetraaminobenzene, 3,3', 4,4'-tetraaminodiphenylisopropylidene, 3,3', 4,4'-tetraaminobiphenyl hexafluoroisopropylidene. It is preferred that at least one kind of tetraamine is chosen from the group consisting of diaminobenzidine, 1,2,4,5-tetraaminobenzene, and 3,3', 4,4'-tetraaminodiphenylether.

[0025] Diamine (C) is at least one kind of diamine chosen from the group shown in formula 10.

[0026].



[Formula 10]

[0027] That is, it is at least one kind of diamine chosen from the group consisting 4,4'-(hexafluoroisopropylidene) bis [2-amino-phenol], 3,3'-dihydroxy-4,4'-diaminobiphenyl (hereinafter, it is abbreviated as 3,3'-dihydroxybenzidine), 3,3'-diamino-4,4'-dihydroxybiphenyl, 3,5-diaminobenzoic acid, 2, 4-diaminophenol, bis (4-amino-3-carboxyphenyl) methane, preferably at least one kind of diamine chosen from 4,4'-(hexafluoroisopropylidene) bis [2-amino phenol], 3,3'-dihydroxybenzidine, 3,3'-diamino-4,4'-dihydroxybiphenyl.

[0028] The more preferred poly (imidazopyrrolone-imide) copolymer stated in the present invention is the copolymer that has undergone polycondensation of the amine component (D) containing at least one kind of tetraamine (B) selected from diaminobenzidine, 1,2,4,5-tetraaminobenzene, and 3,3', 4,4'-tetraaminodiphenyl and at least one kind of diamine (C) chosen from 4,4'-(hexafluoroisopropylidene) bis [2-aminophenol], 3,3'-dihydroxybenzidine), 3,3'-diamino-4,4'-dihydroxybiphenyl with 6FDA at the molar quantity equal thereto.

[0029] The amine component (D) used in the present invention is characterized in that the tetraamine (B) and the diamine (C) are the required components thereto, and the blending mole ratio of (B) and (C) in the amine component is preferably between 7/3~3/7, more preferably between 7/3~4/6. The total molar quantity of (B) and (C) is 30%~100% of the total molar quantity of the amine component (D), and preferably is between 50%~100%.

[0030] As the amine components other than the tetraamine (B) and diamine (C) contained in the

amine component (D) that can be used for this invention, a tetraamine other than (B) and a diamine other than (C) can be used as long as it reacts with the dianhydride, and is a bifunctional amine that generates a polymer which is capable of being formed into a membrane. As the triamine, for example, 1,3,4-triaminobenzene, 3,4,4'-triaminodiphenyl ether are preferred.

[0031] Moreover, essentially all diamines generally used for polyimide polymerization can be used as the diamine. Concretely, for example, at least one kind chosen from the following group can be used: phenylenediamines such as m-phenylenediamine, those having a hydrogen atom of this benzene ring framework substituted by an alkyl group, a hydroxyl group, a carboxyl group, a nitro group, an alkoxy group, and a halogen, for example 2, 4-diaminotoluene, 2,5-dimethyl -1, 4-phenylenediamine, 2,4, 6-trimethyl -1, 3-phenylenediamine, 2-chloro -1, 5-phenylenediamine, 2-methoxy -1, 4-phenylenediamine, 2-chloro-5-methyl-1, 4-phenylenediamine, 3-fluoromethyl-1, 5-phenylenediamine etc., and their various isomers, 1,5-naphthalenediamine, 9, 9-bis (4-aminophenyl) fluorine, 9,10-bis (4-aminophenyl) anthracene, 2, 6-diamino anthraquinone, 1, 5-diamino anthraquinone, 3, 3'-dimethyl naphthidine,

[0032] Also, those with part of the diamine component substituted or their benzene ring hydrogen bonded with more than two benzene rings by an ether group, a thioether group, a carbonyl group, a sulfone radical, a sulfide radical, a methylene group, an isopropylidene radical, a hexafluoroisopropylidene radical by a part of diamine components combined by an amino group, an amide group, etc., or their benzene ring hydrogen with an alkyl group, an aryl group, an alkoxy group, a halogen, and a carboxyl group, etc. For example, they include 4,4'- diamino diphenyl ether, 3, 4'-diamino diphenyl ether, 4,4'- diamino benzophenone, 4, 4'-diamino diphenyl sulfone, 4, 4'-diamino -2, 2'-dimethyl diphenyl sulfone, 4, 4'-diamino -3, 3'-dimethyl diphenyl sulfone, 4,4'- diamino diphenyl sulfide, 4, 4'-diamino diphenylmethane, 4,4'- diamino -3, 3'-dimethyl diphenylmethane, 4, 4'-diamino -3, 3', 5, 5'-tetramethyl diphenylmethane, 4, 4'-diamino -3, 3'- dichlorodiphenylmethane, 2, 2-bis (4-aminophenyl) propane, 2, 2-bis (4-amino -3, 5-diethyl phenyl) propane, 2, 2-bis (4-amino -3, 5-dimethylphenyl) propane, 2, and 2-bis (4-amino-3-methyl-5-ethyl phenyl) propane.

[0033] 2, 2-bis (4-amino-3-methylphenyl) propane, 2, 2-bis (4-aminophenyl) hexafluoropropane, 2, 2-bis (3-aminophenyl) hexafluoropropane, 4, 4'-diamino benzanilide, O-toluidine sulfone, dibenzothiophene -3, 7-diamine -5, 5'-dioxide, 3, 6-diaminocarbazole, 2, 7-diaminofluorene, bis [4-(4-aminophenoxy) phenyl] sulfone, bis [4-(3-aminophenoxy) phenyl] sulfone, 4, 4'-bis (4-aminophenoxy) biphenyl, 2, 2-bis [4-(4-aminophenoxy) phenyl] hexafluoropropane, 1, 4-bis (4-aminophenoxy) benzene, 1, 3-bis (4-aminophenoxy) benzene, 2, 2-bis [4-(4-aminophenoxy) phenyl] propane, 2, 2-bis (3-amino-4-methylphenyl) hexafluoropropane, 2, 2-bis [4-(4-aminophenoxy) phenyl] hexafluoropropane etc., and the hydrogen of benzidine or a benzidine structure substituted by an alkyl group, a halogen, an alkoxy group, a trifluoromethyl radical, etc;

for example they include 2, 2', 6, 6'- trimethyl benzidine, 3, 3'-dimethyl benzidine, 3,3'-dimethoxy benzidine, 2, 2'-dichloro -5, 5' - dimethoxy benzidine, 2, 2'-bis (trifluoromethyl) benzidine, and other amino functional silanes.

[0034] Furthermore, as the polymer used for forming the polymer layer having a close layer as set forth in the present invention, a blended polymer that is blended with adequate polyamide in the poly (imidazopyrrolone-imide) copolymer of the present invention as required can be adequately used. As the polyamide suitable for blending, a polyamide polymerized with the tetraamine and the diamine used in the poly (imidazopyrrolone-imide) copolymer of the present invention is preferred. The blending can be easily carried out by dissolving both components into a satisfactory solvent suitable for yarn spinning doping, to be described later, in the precursor state of the poly (imidazopyrrolone-imide) copolymer of the present invention

[0035] There is no special limit on the production method of the separation membrane having a close layer composed of a poly (imidazopyrrolone-imide) copolymer of the present invention, the form of the membrane and the shape of the membrane. For the separation membrane of the present invention, examples are, the wet yarn spinning method, dry yarn spinning method, dry and wet yarn spinning method, superaqueous expansion method, solvent cast method, and interfacial polymerization. In addition, as the form of the membrane, the asymmetric membrane form which retains a good balance of the properties of strength, endurance, and gas permeability/selectivity required is preferred as a separation membrane. As such an asymmetric membrane, for example, a composite film which holds an asymmetric membrane or close layer composed of the same raw material for the close layer and the porous supporting layer on a porous supporting layer composed of a the raw material different from that of the close layer is preferred. Moreover, as the membrane shape, flat film, tubular, and hollow yarn shape are all acceptable. However, hollow yarn membrane that has a large membrane area in small overall area is preferred. The most preferred mode of the present invention is the hollow yarn composite membrane shape.

[0036] The formation position of the close layer is not especially limited, for example, it may be formed on the surface of one side or the surface of both sides. It is preferred that it is formed on the surface of one side of the film. The close layer stated in the present invention is a delicate thin membrane layer with the mechanism of the membrane permeability to non-agglutinative gas such as oxygen, nitrogen, and hydrogen, essentially only existing as continuous holes and controlled by a hole diameter under the Knudsen effusion rate. The hole opening ratio of the continuous holes is under  $1 \times 10^3$  by area ratio, preferably under  $1 \times 10^4$ , more preferably under  $1 \times 10^6$ , and most preferably there is essentially no presence of continuous holes, representing a tight thin membrane layer controlling the dissolving-diffusion rate. The thinner the thickness, the better, preferably between  $2 \mu\text{m}$ ~ $0.02 \mu\text{m}$ , more preferably between  $0.5 \mu\text{m}$ ~ $0.02 \mu\text{m}$ , and

most preferably between  $0.1\ \mu\text{m}$  ~  $0.02\ \mu\text{m}$ . The hole diameter of the continuous holes existing in the close layer is less than the retention diameter for Knudsen effusion, which can be easily verified by the ratio of the membrane permeating speed in the case of an oxygen and nitrogen mixture for gas separation being in the range of error above 0.935.

[0037] The heterogeneous film or the composite membrane of this invention consists of a polymer macromolecule layer essentially having a close layer and a porous supporting layer. The polymer layer is formed from a poly (imidazopyrrolone-imide) copolymer, and the porous supporting layer is the same polymer in the case of heterogeneous film, and is formed from an essentially different polymer in the case of a composite membrane. The form of the membrane of the polymer layer essentially having a close layer as set forth in the present invention may be a homogenous structure. However, the asymmetric membrane structure which has a porous layer supporting the thin close layer (which becomes the active separation layer) is preferred. It is preferred that the porous structure part of the polymer layer composed of the poly (imidazopyrrolone-imide) copolymer has extremely low resistance to the gas permeation with [respect to] the close layer, and each micro-hole forming the porous structure part is essentially a continuous hole. Moreover, the thickness of the polymer layer is 5%~50% of the total film thickness, which is preferably  $5\sim 30\ \mu\text{m}$ .

[0038] This invention also provides a hollow yarn composite film having the most suitable dimensions for each of the practical applications. For example, in case of practical use for separation of oxygen and nitrogen in the air using the internal pressurization method, it can provide a hollow yarn composite membrane preferably with the inner diameter of the hollow yarn between  $130\ \mu\text{m}$ ~ $400\ \mu\text{m}$ , the outer diameter between  $200\ \mu\text{m}$ ~ $800\ \mu\text{m}$ , which essentially provides the physical strength of the hollow yarn membrane, and the membrane thickness of the porous supporting layer is preferably between  $40\ \mu\text{m}$ ~ $300\ \mu\text{m}$ , based on the constraint elements such as film strength, durability, pressure loss of the compressed air, and yarn occupancy cross-sectional area (modular magnitude).

[0039] The porous supporting layer of the hollow yarn composite membrane of the present invention is characterized in that the porous supporting layer membrane is tightly adhered to the polymer layer composed of the poly (imidazopyrrolone-imide) copolymer, it has excellent physical properties, such as sufficient mechanical strength to endure actual use of the membrane and heat resistance, excellent chemical properties such as chemical resistance and weatherability, and a great number of continuous fine holes are formed in order to minimize permeation resistance of various separation objects. It is not particularly limited in the shape of the fine pores and the rate [spacing] of pores. The so-called finger-like shape and/or sponge-like shape are acceptable.

[0040] Moreover, for most cases, since the poly (imidazopyrrolone-imide) copolymer is

practically not dissolvable in ordinary solvent, after producing the film using the precursor of the solvent soluble poly (imidazopyrrolone-imide) copolymer, by heat treatment of the precursor and carrying out polymerization of imidazopyrrolone-imide, it is desired that the resin for forming the porous supporting layer membrane has sufficient heat resistance to endure such heating treatment. As the preferred resins suitable for the porous supporting layer membrane having these properties, examples are a mixture or copolymer consisting of at least one kind of resin chosen from aromatic polyamide resin, polysulfone resin, polyimide resin, polyetherimide resin, polyamidoimide resin, polybenzimidazole resin, polybenzoxazole, polybenzothiazole, polyquinoxaline, and polypiperazine, etc. Moreover, the poly (imidazopyrrolone-imide) copolymer may be further mixed to these resins if needed.

[0041] A mixture which consists of at least one kind of resin chosen from polyimide resin, polysulfone resin, polybenzimidazole resin, and aromatic polyamide resin, is preferred. It is more preferred that it is the aromatic polyamide resin or a mixture containing the aromatic polyamide resin and polyimide resin and/or polysulfone resin, and it is most preferred that it is a mixture of the aromatic polyamide resin with the polyimide resin.

[0042] The polysulfone resin mentioned here is essentially an amorphous polymer having a molecular weight that allows formation of films, structured by repeating the units of the para-phenylene unit and/or paraphenylene unit bonded by a sulfone group, ether group and/or isopropylidene group. For example, it includes polysulfone, polyethersulfone, and polyallylsulfone, etc.

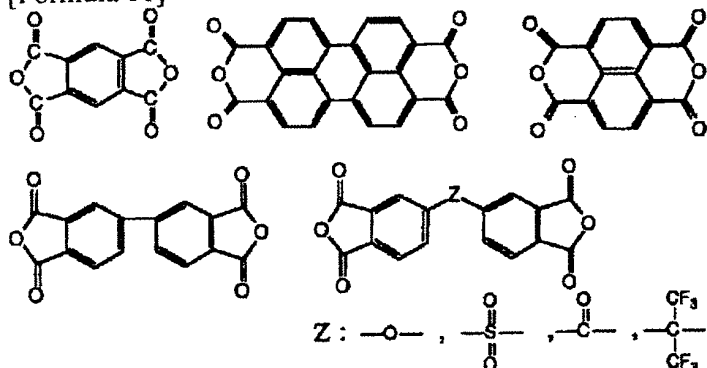
[0043] Moreover, the polyamide resin that forms the porous supporting layer membrane of the hollow yarn composite membrane mentioned here may be soluble or insoluble to a solvent. The solvent-insoluble polyamide can form a porous layer comprising solvent-insoluble polyamide by heating or irradiation by ultraviolet rays after film formation, using a soluble precursor such as a polyamide, polyamide acid, or polyisoimide dopant.

[0044] Moreover, in order to block the few pinholes (continuous fine pores) generated on the close layer of the composite membrane if needed, surface coating or filling treatment of the close layer may be conducted with a raw material with high gas permeability such as silicone and polyacethylene. In order to further improve selectivity of the gas, surface treatment or plasma treatment may be conducted on the close layer with chlorine gas, fluorine gas, a chlorine compound, a fluorine compound, etc.

[0045] Moreover, this invention provides an excellent production method for hollow yarn composite membrane as the second invention. That is, after polymerizing at least one kind of tetracarboxylic acid dianhydride (A) chosen from formula 11, with the amine component (D) containing

[0046]

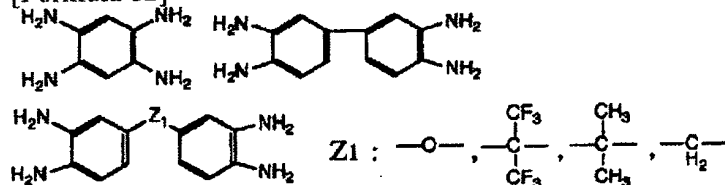
[Formula 11]



[0047] at least one kind of tetraamine (B) chosen from formula 12 at molar quantity equal to the tetracarboxylic acid dianhydride,

[0048]

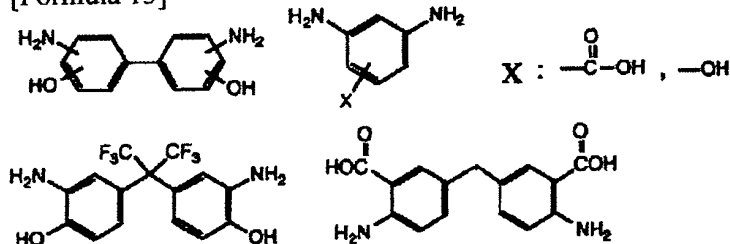
[Formula 12]



[0049] [text incorporated in paragraph [0051] due to Japanese text structure]

[0050]

[Formula 13]



[0051] and at least one kind of diamine (C) chosen from formula 13, as a required component, the essentially solvent soluble poly (imidazopyrrolone-imide) copolymer precursor dopant (a) and the polymer dopant (b) used for forming the porous supporting layer membrane are coextruded in a hollow yarn shape with multi-layer structure at the same time using a multiple circular ring nozzle. Then, after allowed contact with a congealed liquid and coagulation, copolymerization of the poly (imidazopyrrolone-imide) copolymer is carried out by heating the precursor. The present invention provides a production method of a hollow yarn composite

membrane of the poly (imidazopyrrolone-imide) copolymer having a close layer comprising the poly (imidazopyrrolone-imide) copolymer.

[0052] According to the manufacturing approach of this invention, the hollow yarn composite membrane having a polymer layer composed of a poly (imidazopyrrolone-imide) copolymer essentially comprising a close layer and a porous supporting layer membrane formed with different polymer from the copolymer raw material can be offered at the industrial manufacturing level.

[0053] The polymer layer composed of the aforementioned poly (imidazopyrrolone-imide) copolymer may be the so-called asymmetric structure having a close layer essentially with no continuous pores, which becomes the active separation layer of the separation object material with the porous structure part. Also, the homogeneous structure obtained in the polymer layer by adequately adjusting the solvent composition of the yarn spinning dopant, and the condition of yarn spinning formed with a close layer only, is also acceptable. The asymmetric structure polymer layer is more preferred, from the viewpoint that the close layer can be produced thinner.

[0054] The dopants (a) used in the present invention are those polymerized from the aforementioned tetracarboxylic acid dianhydride (A) with the amine component (D) comprising the tetraamine (B) and the diamine (C) as the required components, and the precursor of the poly (imidazopyrrolone-imide) copolymer is dissolved in a solvent. The precursor mentioned here is a polymer that forms the polymer layer having a tight separation layer composed of the poly (imidazopyrrolone-imide) copolymer by final heating. It is essentially dissolvable in an organic solvent, capable of forming a film by congealed liquid solidification and it is acceptable that the polymer changes to poly (imidazopyrrolone-imide) copolymer by applying adequate heating. For example, the polymer having at least one type of structure such as polyimide, polyamide, polyisoimide, and polyimidazol is preferred. Needless to say the present invention includes, but is not limited to, these examples, and any structure of the precursor is acceptable.

[0055] Generally, these precursors are obtained by adding more than one kind of reaction adjuvant, such as a pyridine, a benzoic acid, an acetic anhydride, a triethylamine, a trifluoroacetic acid anhydride, a thionyl chloride, and a dicyclocarbodiimide, and carrying out the polymerization of the amine component (D) with an equimolecular amount of the above-mentioned tetracarboxylic dianhydride (A) if needed, in the presence of a reaction solvent, such as N,N-dimethylformamide, N-methyl pyrrolidone, and N,N-dimethylacetamide, to dissolve these monomers.

[0056] The dopant (a) of the precursor of the poly (imidazopyrrolone-imide) copolymer used for yarn spinning of the hollow yarn composite membrane can be used directly to dope solution itself by allowing reaction of the tetracarboxylic acid dianhydride (A) with the amine component (D). Additionally, it may once dope the precursor from the reaction solution as a solid object,

and dope and re-dissolve in an adequate organic solvent. The concentration of the polymer solids of the yarn spinning dopant (a) is preferably 5 wt.%~35 wt.%, and is more preferably 15 wt.%~30 wt.%.

[0057] The dopant (b) used by this invention is dissolved in a solvent in order to form a porous supporting layer membrane. These polymers include the aforementioned solvent soluble polymer. Moreover, it is acceptable to mix a precursor of the poly (imidazopyrrolone-imide) copolymer in to these resins.

[0058] As the polymer of dopant (b), a mixture which consists of at least one kind of resin chosen from polyimide resin, polysulfone resin, polybenzimidazole resin, and aromatic polyamide resin is more preferable. The aromatic polyamide resin, or the mixture of aromatic polyamide resin, polyimide resin, and/or polysulfone resin are still more preferred, and the mixture of aromatic polyamide resin and polyimide resin are the most preferred.

[0059] The concentration of the polymer solid of the dopant (b) which forms the porous supporting layer is preferably between 10 wt.% - 35 wt.%, and more preferably between 15 wt.% - 30 wt.%. It is not especially limited as long as the solution viscosity of the dopant can carry out the wet yarn spinning.

[0060] The solvent which can be used for the dopant (a) and (b) of this invention dissolves the resin which forms the aforementioned precursor and the porous supporting layer, and those that have compatibility with a coagulation liquid, to be described later, can be used. For example, it includes alkyl halides such as dichloromethane, chloroform, and 1,1,2-trichloroethane; halogenated phenols such as the orthochlorophenol, parachlorophenol, and dichlorophenol; amide series solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, and N-methyl pyrrolidone; sulfur series solvents such as dimethyl sulfoxides and sulfolane; and at least one type of organic solvent such as hexamethylphosphoric triamide,  $\gamma$ -butyl lactone, and dioxane.

[0061] Moreover, for the purpose of improvement in dopant stability, and spinnable properties, improvement in gas transparency and the selectivity of the composite membrane, the low molecular weight polyethylene glycol, polypropylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone; a volatile component such as an acetone; a tetrahydrofuran; a weak solvent such as a toluene, a xylene, and an acetic acid; a water-soluble polyhydric alcohol such as ethylene glycol, glycerin; inorganic salts such as lithium chloride, lithium bromide, potassium chloride, potassium bromide, and magnesium bromide; the amine group such as triethylamine, tributylamine, and a dipropyl amine, small quantities of alcohols such as methanol, ethanol, n-propanol, isopropanol, minerals and water, etc. can be added to the dopant (a) and (b) if needed.

[0062] In this invention, the dopant (a) and (b) are extruded from a multiplex circular ring nozzle into a hollow yarn shape. The multiplex circular ring nozzle used by this invention can be those well-known. A model diagram of the desired nozzle is shown in FIG. 1. In the drawing, "1" is



the opening of the nozzle core part which extrudes the gas or liquid (hereinafter called the core material) mainly for maintaining the configuration of the hollow yarn, and "2" and "3" are slits which allow the dopant (a) or (b) in the drawing to flow out. When manufacturing the composite membrane which has a porous supporting layer on the inner side of the composite hollow yarn membrane and a polymer layer having a close layer on the outside, the core material is allowed to flow out from "1", the dopant (b) is extruded from "2", and dopant (a) is extruded from "3" at the same time. When producing a composite membrane having a porous supporting layer membrane on the outside part, and a polymer layer on the inside part, the core material is allowed to flow out from "1", the dopant (b) is extruded from "2", and dopant (a) is extruded from "3" at the same time. By so doing, a hollow yarn composite membrane having a multiple layer structure of more than two layers can be formed according to the number of slits at the multiplex circular ring nozzle.

[0063] According to the production method of the present invention, for example, by adequately selecting the composition, temperature, and concentration of the dopant solution, the composition of the fluid in the inner pipe, and the yarn spinning conditions, the close layer may be formed on the surface of the inner side and/or the outside of the hollow yarn. Among these [options], the composite film formed with the close layer on the outside surface of the hollow yarn, for example, first extruding the dopant in a gas phase, then immersing it in a congealed liquid for solidification, that is, the well-known dry and wet method, can be easily produced. This method is preferred from the aspects of mass productivity, gas permeability and selectivity of the resultant composite film. In addition, the dimension of the hollow yarn composite membrane can be adequately adjusted by the extruded amount of the dopant, the dimension of the nozzle, and the yarn spinning draft, and the outer and inner diameter can be adjusted adequately to meet the needs of actual usage.

[0064] The fluid used as the core material when extruding the dopant into a hollow shape may be in gas state or liquid state. For example, gases such as nitrogen and air can be used, or water, propanol, ethanol, methanol, glycerols, or a mixture of these liquids. Moreover, inorganic salts such as lithium chloride, lithium bromide, and potassium chloride; a resin solvent resin such as N-methyl pyrrolidone and N,N-dimethylacetamide, and a poor resin solvent such as acetone, methyl ethyl ketone, xylene, toluene, and acetic acid can be suitably added to these liquid core materials if needed.

[0065] The ambient atmosphere for extruding a dopant may be the gaseous phase of air or nitrogen, and it may be a vaporous ambient atmosphere such as in the presence of a solvent. The ambient atmosphere can be adjusted by adequately adjusting the temperature and humidity if needed.

[0066] The polymer dopant of multilayer structure co-extruded from a multiplex circular ring

nozzle in the shape of a hollow yarn can be completely solidified by contact with a coagulation liquid. The coagulation liquid can use a liquor mixture blended with one or more types chosen from the lower alcohols, such as N-propanol, isopropanol, methanol, and ethanol, acetone, water, etc. The preferred liquid mixture is with water or with water and another organic solvent. Moreover, the hydrogen ion concentration of water or a water solution may be adjusted if needed. Using heat treatment, the hollow yarn composite membrane consisting of a two-layer structure of the polymer layer has the close layer composed of the precursor of the poly (imidazopyrrolone-imide) copolymer obtained in this manner, and the porous supporting layer membrane, are allowed to condensation polymerize, leading to polymerization of the poly (imidazopyrrolone-imide). The heating condition is the condition where the close layer of the precursor essentially changes to poly (imidazopyrrolone-imide) copolymer. The porous structure of the polymer forming the porous layer is subject to the condition where there is essentially no occurrence of denaturalization. It is preferred that the heating treatment is carried out at 200°C~450°C, more preferably at 250~400°C, under a reduced pressure or in an inert gas for 30 min ~ 24 hours, preferably between 2 and 8 hours. The reduced pressure mentioned here is a reduced pressure atmosphere below 200 Torr, preferably below 20 Torr, as long as the resin constituting the hollow yarn composite membrane is essentially not influenced by thermal deterioration due to oxidation during the thermal treatment. Additionally, nitrogen, argon, helium, etc. are mentioned as suitable as inert gas.

[0067] The heating process may be carried out by continuous heat treatment of the hollow yarn composite membrane obtained by coagulation, and heat-treatment may be performed with the bundle of hollow yarn composite membrane arranged in suitable length, and it also may be performed after modularization.

[0068] The change from the precursor to the poly (imidazopyrrolone-imide) copolymer by heat treatment can be easily verified by infrared absorption spectrum. Moreover, as for the organic solvent and the various additives which remain in the resultant composite membrane, it is essentially preferred to remove them, and the removal process can be carried out by well-known methods such as conduction heating under vacuum after washing with warm water and/or a low boiling point solvent to dissolve the solvent residue. It is preferred that the removal of the organic solvent residue, especially the solvent used for the dopant, is performed between the heating treatment process because of polyimidazopyrrolone.

[0069] [Embodiment of the Invention] In the case of the composite membrane, this invention performs equimolecular quantity partial condensation polymerization of above-mentioned tetracarboxylic dianhydride (A) and an above-mentioned amine component (D), which is melted into a solvent to produce a yarn spinning dopant used for the close layer, and the resin for forming the porous layer is dissolved in a solvent to produce a yarn spinning dopant for the

porous layer; they are co-extruded from a multi-circular ring nozzle, and the extruded hollow yarn composite membrane is heat treated. The resultant hollow yarn membrane may be modulated and used as an air separation membrane for producing nitrogen or oxygen enriched air and degassing of water.

[0070] [Application example] The present invention is described in further detail according to the application examples below.

[Application example 1] Dissolve 0.15 mol diaminobenzidine [tetraamine (B)] and 0.15 mol 3,3'-dihydroxybenzidine [diamine (C)] as the amine component (D) in 1000 g anhydrous treated N,N'-dimethylacetamide (hereinafter abbreviated as DMAC). Then while ice-cooling this solution, slowly drop 850 g DMA solution dissolved of 0.3 mol 6FDA as the tetracarboxylic acid dianhydride (A). After dropping is complete, stir for four hours while ice-cooling, then add about 0.9 molar quantity pyridine to this solution, after stirring thoroughly, then add about 0.9 molar quantity acetic anhydride and stir for 3 more hours. The resultant reaction solution is dropped in a large quantity of water to separate the solids. The solids obtained are further cleaned with a large amount of water several times; after solvent substitution is complete, the solids are thoroughly dried in a vacuum oven at about 100°C, and the precursor solid of the poly (imidazopyrrolone-imide) copolymer is obtained. The resultant solid is dissolved in DMAC with a small amount of isopropyl alcohol added in 24 wt parts; it is then filtered with a stainless filter with hole diameter 20 µm, then subjected to reduced pressure defoaming, and yarn spinning dopant (a) is obtained. Dissolve Matrimide 5218 (made by Ciba Geigy Co., dissolvable polyamide), and Conex (Teijin, Ltd.: poly meth phenylene isophthalamide) to 25 wt parts DMAC at 4/6 weight ratio, filter with a stainless filter with hole diameter 20 µm, carry out reduced pressure defoaming, and yarn spinning dopant (b) is obtained. These dopant solutions are discharged using a multiple circular pipe nozzle with  $\phi$  □.□□□□.□□□□.□□□□.□□□□.□□□□.□□□□ from the pipe outer diameter while running water from the central part of the pipe at a discharge rate of about 3.2 g/min for the dopant (b) to form the porous supporting layer of the composite membrane from the inside circular ring, and at a discharge rate of about 0.7 g/min for the dopant solution (a) of the poly (imidazopyrrolone-imide) precursor heated at about 50°C from the outside circular ring at the same time in an air atmosphere. Then, 65/35 wt parts isopropyl alcohol continuously adjusted to 5°C is introduced to a congealed liquid mixture, and coagulation is allowed, and then continuous winding onto a bobbin at a winding rate of about 20 m/min. After immersing the obtained hollow yarn in running water and thoroughly washing it, drain the water, and allow to dry. Then dip in a liquor mixture of 7/3 wt parts of water/isopropyl alcohol overnight, vacuum drying thoroughly at about 120°C. Then, heat treatment is performed at 350°C in vacuum for 8 hours, and this precursor is converted into the poly (imidazopyrrolone-imide). The hollow yarn composite membrane obtained is a hollow yarn composite membrane

having a close layer on the outer surface of the hollow yarn, with a ratio of the thickness of the inner side porous supporting layer of the hollow yarn/the thickness of the outer poly (imidazopyrrolone-imide) layer of the hollow yarn of about 6:1, through microscope observation of the cross section of the hollow yarn with inner diameter about 220  $\mu\text{m}$ , and outer diameter about 470  $\mu\text{m}$ . The hollow yarn composite membrane has a close layer on the outer surface of the hollow yarn. The permeating speed of each gas through the hollow yarn composite membrane obtained was measured using the pressure method according to ASTM D1434 at 25°C atmosphere  $\Delta P$ =about 2 [ $\text{kg}/\text{cm}^2$ ] using the pure gases, respectively. The results are shown below.

Oxygen:  $2.71 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.28 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0071] [Application example 2] Dissolve 0.15 mol of diaminobenzidine [tetraamine (B)], 0.09 mol 3, 3'-dihydroxybenzidine [diamine (C)], and 0.06 mol 9, 9-bis (4-aminophenyl) fluorene [other amines] as the amine component (D) in 1200 g DMAC. Then ice cool this solution while slowly dropping a solution of 850 g DMAC dissolved with 0.3 mol 6FDA as the tetracarboxylic acid bianhydride (A) while stirring the solution. After dropping is complete, stir for four hours under ice cool conditions. Then add 0.9 molar amount of pyridine to this solution, and stir thoroughly. Next add 0.9 molar quantity of acetic acid anhydride and stir for 3 hours. The resultant reaction solution is dropped in to a large amount of water, and the solids are separated. Then further wash several times with a large amount of water, and after carrying out through solvent substitution, these solids are dried in a vacuum oven at about 100°C, and the solids of the precursor for poly (imidazopyrrolone-imide) are obtained. The yarn spinning dopant (a) is adjusted by using the precursor of the obtained (imidazopyrrolone-imide) copolymer, otherwise, the hollow yarn composite membrane having a close layer composed of a poly (imidazopyrrolone-imide) copolymer is obtained with the identical method as in application example 1. The oxygen permeation speed and nitrogen permeation speed of the hollow yarn composite membrane were measured with the same method as in application example 1. The results are shown below.

Oxygen:  $6.67 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.76 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Carbon dioxide:  $33.24 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0072] [Application example 3] Under a nitrogen gas atmosphere, dissolve 0.12 mol diaminobenzidine [tetra-amine (B)] and 0.12 mol 3,3'-diamino -4, 4'-dihydroxy biphenyl [diamine (C)] as the amine component (D) at room temperature, and 0.06 mol 9,9-bis (4-aminophenyl) fluorine [other amines] in 1000g DMAC which has been dehydration processed,

then while ice-cooling this solution, slowly drop 850g DMAC dissolved with 0.3 mol 6FDA as the tetracarboxylic dianhydride (A). After stirring for 6 hours, and ice-cooling after dropping is complete, the resultant reaction solution was dropped in to a large amount of water, and the solids were separated. After washing the solids obtained with a large amount of water several times and carrying out complete solvent substitution, these solids were dried in about 100°C vacuum oven, and the precursor solid of the poly (imidazopyrrolone-imide) copolymer was obtained. Dissolve the resultant solids in 25 wt. parts DMAC with a small amount of isopropyl alcohol added, filter with a stainless filter with hole diameter 20  $\mu\text{m}$ . Then carry out reduced pressure deformation, and the yarn spinning dopant (a) is obtained.

[0073] Except that it is prepared by using the precursor of the (imidazopyrrolone-imide) copolymer obtained as yarn spinning dopant (a), the hollow yarn composite membrane having a close layer composed of the poly (imidazopyrrolone-imide) copolymer is obtained by using the identical method as in application example 1.

Oxygen:  $3.10 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.33 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0074] [Application example 4] Except that 0.15 mol diaminobenzidine [tetraamine (B)] and 0.15 mol 4,4'-( hexafluoroisopropylidene) bis [2-aminophenol [diamine (C)] were used as the amine component (D), the precursor solids of the poly (imidazopyrrolone-imide) copolymer were obtained in the same manner as in application example 1. The resultant solids are dissolved in a DMAC with a small amount of isopropyl alcohol in 25 wt. parts added, and then filtered with a stainless filter with hole diameter 20  $\mu\text{m}$ , then subjected to reduced pressure defoaming, and the yarn spinning dopant (a) is obtained. Dissolve Matrimid 5218 / Conex / Redel [transliteration] A-100 (made by Amoko Performance Products Co, polyethersulphone) in 25 wt. parts DMAC at 3/6/1 weight ratio, filter with a stainless filter with hole diameter 20  $\mu\text{m}$ , carry out reduced pressure deformation, and the yarn spinning dopant (b) is obtained. The hollow yarn composite membrane having a close layer compose of poly (imidazopyrrolone-imide) copolymer is obtained using the same method as in application example 1, other than using the above mentioned yard spinning dopant (a) and (b). The permeating speed of oxygen and nitrogen [is measured] with the same method as in application example 1. The results are shown below.

Oxygen:  $3.59 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.51 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0075] [Application example 5] The yarn spinning dopant (b) was prepared as polybenzimidazole / Conex / DMAC=10/16/74 wt.%, and the hollow yarn composite membrane

was obtained by the same method as in application example 1, except for heat-treating at 300 degrees C for 6 hours. In addition, the polybenzimidazole used is the polymer obtained by polymerization of the diaminobenzidine and the isophthalic acid using a conventional method. The oxygen permeation rate and nitrogen permeation rate of the hollow yarn composite membrane were measured by the same method as in application example 1. The results are shown below.

Oxygen:  $3.25 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.38 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[Application example 6] The yarn spinning dopant (b) was prepared with the solution of the Conex (Teijin, Ltd.: polymetaphenylene isophthalamide) / NMP/ isopropyl alcohol =20/81/1 weight parts, and the hollow yarn composite membrane was obtained by the same approach as in application example 1 except for heat-treating at 300°C for 5 hours. The oxygen permeation rate and nitrogen permeation rate of the hollow yarn composite membrane were measured by the same approach as in application example 1. The results are shown below.

Oxygen:  $2.12 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.26 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0076] [Application example 7] Except that 0.06 mols 1, 2, 4, 5-tetraaminobenzene [tetraamine (B)], 0.18 mol 3, 3', 4, 4' tetraamino diphenyl ether [tetraamine (B)], 0.06 mol 3,3'-diamino -4,4'-dihydroxybenzidine [diamine (C)] were used as the amine component (D), the hollow yarn composite membrane was obtained by the same approach as in application example 1, except that the poly (imidazopyrrolone-imide) copolymer precursor polymerized with the same method as in application example 1 is used as yarn spinning dopant (a). The oxygen permeation rate and nitrogen permeation rate of the hollow yarn composite membrane were measured by the same approach as in application example 1. The results are shown below.

Oxygen:  $1.54 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.18 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

[0077] (Comparative example 1) The solids of the precursor of the poly (imidazopyrrolone-imide) copolymer were obtained by the same approach as in application example 1 except using 0.15 mol of diaminobenzidine, and 0.15 mol of 2,2-bis [4- (4-amino phenoxy)] hexafluoropropane as the amine component. The hollow yarn composite membrane which has a close layer consisting of a poly (imidazopyrrolone-imide) copolymer was obtained with the same method as in application example 1, except the precursor of the poly (imidazopyrrolone-imide) copolymer is used in the yarn spinning dopant (a).

[0078] The oxygen permeation rate and nitrogen permeation rate of the hollow yarn composite membrane were measured by the same approach as in application example 1. The results are shown below.

Oxygen:  $5.90 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $1.24 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

As mentioned above, absence of the diamine (C), which is the indispensable component of this invention, in an amine component (D), leads to a low separation factor of oxygen and nitrogen.

[0079] (Comparative example 2) Dissolve 0.3 mol of 3, 3'-dihydroxybenzidine in 950g DMAC, which has undergone dehydration processing, at room temperature under nitrogen-gas-atmosphere. Then, add 0.3 mol fine particles of 6FDA divided into 5 portions in every 10 minutes, stirring under a nitrogen gas atmosphere. Then further stir at room temperature for 2.5 hours after the substance addition is complete. Add 1000g DMAC to this reaction solution after this, and add 1.2 molar quantity acetic anhydride and 1.2 molar quantity of pyridine, after stirring for 1 hour at room temperature; increase the temperature to 55°C and stir for two more hours. After cooling to near room temperature, the reaction solution obtained is dropped into a large quantity of isopropanol, filtered, and the solids separated. The solids obtained are washed thoroughly with a large amount of ethanol, and [dried] in about 100°C vacuum oven, and the polyimide powder is obtained. The hollow yarn composite membrane which has a close layer consisting of a polyimide was obtained by the same approach as in application example 1 except for using this polyimide for the yarn spinning dopant (a). The oxygen permeation rate and nitrogen permeation rate of the hollow yarn composite membrane were measured by the same approach as in application example 1. The results are shown below.

Oxygen:  $0.88 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $0.11 \times 10^{-5}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

As mentioned above, it is clear that the gaseous transmission rate is low for the compact layer consisting only of a polyimide.

[0080] (Comparative example 3) Dissolve 3, 4, 4'-triaminodiphenyl ether in 50g DMAC, which has undergone dehydration treatment with of 10 millimols diaminobenzidine at room temperature under a nitrogen gas atmosphere and add 10 millimols triethylamine to this liquid solution. Then, while ice cooling this solution, slowly drop 50 g DMAC solution dissolved in 10.1 millimols of 6FDA; after dropping is complete, continue to stir for 4 hours while cooling in a ice water bath. Then flow cast the obtained polymerization solution in a Petri dish, dry in a dryer at 70°C for 4 hours, then after thermal treatment of the film in a vacuum at 200°C for 4

hours, conduct further thermal treatment for 4 hours at 330°C in a vacuum. A film in the thickness of about 27  $\mu\text{m}$  is obtained. The permeability coefficient of the obtained film for oxygen and nitrogen was measured with the pressure method according to ASTM D1434 at 25°C atmosphere  $\Delta P$ =about 2 [ $\text{kg}/\text{cm}^2$ ] using the pure gases, respectively. The results are shown below.

Oxygen:  $5.68 \times 10^{-10}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $1.04 \times 10^{-10}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

As mentioned above, it is clear that when the required component diamine (C) is absent in the amine component (D), the separation factor of oxygen and nitrogen is low.

[0081] (Comparative example 4) Dissolved 10 millimol 1, 2, 4, 5-tetraaminobenzene in 60g DMAC, which has undergone dehydration processing, at room temperature under nitrogen gas atmosphere, and add 10 millimols triethylamine to this solution. Then, while ice-cooling this solution, 50g of DMAC solution dissolved in 10.1 millimols 6FDA is dropped slowly, and stirred for 4 hours in an ice water bath after dropping is complete. Then flow cast the obtained polymerization solution in a petri dish, dry in a dryer at 70°C for 4 hours, then after thermal treatment of the film in a vacuum at 200°C for 4 hours, conduct further thermal treatment for 4 hours at 330°C in a vacuum. The obtained film is brittle and cracks easily. The gas permeability property measurement could not be carried out.

(Comparative example 5) Dissolve 5 millimols diaminobenzidine and 0.5 millimols 4,4'-diaminodiphenyl ether in 60g of DMAC solution, which has undergone the dehydration process, then while ice-cooling this solution, slowly drop 50g of DMAC with 10.1 millimols of 6FDA dissolved, and stir for 4 hours in an ice water bath after dropping is complete. Then flow cast the obtained polymerization solution in a Petri dish, dry in a dryer at 70°C for 4 hours, then after thermal treatment of the film in a vacuum at 200°C for 4 hours, conduct further thermal treatment for 4 hours at 330°C vacuum. The permeability coefficient of the oxygen and nitrogen of the obtained film was measured with the pressure method according to the ASTM D1434 at 25°C atmosphere  $\Delta P$ =about 2 [ $\text{kg}/\text{cm}^2$ ] using the pure gases, respectively. The results are shown below.

Oxygen:  $11.31 \times 10^{-10}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

Nitrogen:  $2.21 \times 10^{-10}$  [ $\text{cm}^3$  (STP) /  $\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ]

As mentioned above, it is clear that when the required component diamine (C) is absent in the amine component (D), the separation factor of oxygen and nitrogen is low.

[0082] [Effect of the Invention] It displays excellent gas permeability, separability solvent



resistance, heat resistance, flexibility, and excellent physical properties applicable to films for practical use.

[Brief explanation of the drawing]

[FIG 1.] is a pattern diagram of the multilayer extrusion nozzle [used] to implement this invention. A is a cross-section drawing of the nozzle, B is the shape of the nozzle outlet.

[Explanation of the numbers]

1. The passage for liquid's inner pipe
2. The passage for dopant solution (b)"
3. The passage for dopant solution (a)"

# PHOENIX

## TRANSLATIONS

*...the height of EXCELLENCE...*

Kokai Patent Application No HEI 9[1997]-24260  
POLY (IMIDAZOPYRROLONE-IMIDE) COPOLYMER SEPARATION  
MEMBRANE AND ITS PRODUCTION METHOD

Translated from language into English  
by Phoenix Translations Code No. 142-9670

2110-A WHITE HORSE TRAIL, AUSTIN, TX 78757 Phone: (512) 343-8389  
Toll-free: 877-452-1348, Fax: (512) 343-6721, Email: phoenixtranslations@ev1.net